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by

Bruce A. Tichenor
Air and Energy Engineering Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

AIR AND ENERGY ENGINEERING RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

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16. ABSTRACT The paper discusses the measurement of organic emissions from a variety of indoor materials, using small (166 liter) environmental test chambers. The following materials were tested: adhesives, caulks, pressed wood products, floor waxes, paints, and solid insecticides. For each material, chamber concentration of organics has been determined for a range of environmental conditions (e.g., air exchange rate, temperature, and relative humidity). Various product loading ratios (area of sample/volume of chamber) have also been investigated. Emission rates for individual organic compounds, as well as total measured organics, were calculated. The effects of environmental variables on emission rates have been evaluated. Models are used to evaluate the effect of chamber walls and concentration on emission rates.

17. KEY WORDS AND DOCUMENT ANALYSIS

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Organic Compounds	Waxes	Stationary Sources	07C	11G
Emission	Paints	Indoor Air	14G	11C, 13C
Measurement		Small Chamber Tests	14B	
Adhesives			11A	
Sealing Compounds				

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Bruce A. Tichenor
U. S. Environmental Protection Agency
Air and Energy Engineering Research Laboratory
Research Triangle Park, North Carolina 27711, USA

Abstract

Organic emissions from a variety of indoor materials have been measured using small (166 liter) environmental test chambers. The following types of materials have been tested: adhesives, caulks, pressed wood products, floor waxes, paints, and solid insecticides. For each material, chamber concentration of organics has been determined for a range of environmental conditions (e.g., air exchange rate, temperature, and relative humidity). Various product loading ratios (area of sample/volume of chamber) have also been investigated. Emission rates for individual organic compounds, as well as total measured organics, were calculated. The effects of environmental variables on emission rates have been evaluated. Models are used to evaluate the effect of chamber walls and concentration on emission rates.

Introduction

The U. S. Environmental Protection Agency's indoor air quality research program includes the characterization of sources of indoor air pollutants (12, 13). EPA's Air and Energy Engineering Research Laboratory in Research Triangle Park, North Carolina, is conducting studies in small environmental test chambers to develop organic emissions data on a variety of building materials and consumer products. This research program has several objectives, including: development of testing protocols, determination of emission factors, development of source emission models, and establishment of material/product rankings based on emission characteristics (e.g., emission factors, specific organics emitted) (10).

Test chamber evaluations of emission rates of organic vapors from indoor materials and products have been reported by several investigators (1, 4, 5, 7, 8, 10, 11). The lack of standard testing protocols makes it difficult to evaluate and compare the various emission rates data that have been reported. A number of test conditions are critical to an effective determination of emission rates, including: temperature, humidity, air exchange rate, and product loading (area of sample/volume of test chamber). In addition, the effects of chamber concentration and chamber "wall effects" need to be determined. Finally, the age and condition of the sample affect its emission rate. All of these variables and phenomena are considered in this research program.

Experimental facility

EPA's Indoor Air Source Characterization Laboratory has been described in detail in previous papers (8, 9, 10, 11). The facility consists of the following components: a clean air conditioning and delivery system, an incubator containing two 166 liter environmental test chambers, sampling manifolds, and sample collection adsorbers using Tenax and charcoal. A permeation system for quality control is included. The environmental variables are monitored and controlled via microcomputer. Organic analyses are conducted by thermal desorption, concentration via purge and trap, and gas chromatography (GC) using flame ionization detectors (FID). A separate microcomputer provides GC data analysis. All data are input to spreadsheets for further analysis.

Mechanical tests on the system were performed to determine environmental control capabilities (9). These tests showed that setpoints can be held within the following limits: temperature, $\pm$0.1°C; relative humidity, $\pm$2.0 percent; and airflow, $\pm$0.7 percent of reading.

Experimental procedures

Headspace analysis

Prior to evaluation in the environmental test chambers, materials are evaluated by headspace analysis (6). A sample of material is placed in a 1 liter Teflon lined container which is purged with nitrogen at 50 ml/min for 30 minutes. The exit flow is collected on Tenax and analyzed after thermal desorption. Gas chromatography/mass spectroscopy (GC/MS) analysis provides identification of the compounds contained in the material's emissions. Approximately 10 of the compounds are selected for measurement in subsequent chamber tests.

Chamber testing

Experimental designs are established for each material tested to evaluate the effect of various parameters: temperature, relative humidity, air exchange rate, and chamber loading. Based on the experimental design, environmental setpoints are established and the chambers are purged with clean air for several hours prior to placing samples in the chambers. Several types of materials have been evaluated, and the types of samples used in the chambers varied accordingly: silicone caulk, floor adhesive, and floor wax were spread on aluminum plates; a wood stain was applied to a hardwood (poplar) board that was cut to size; moth crystal cakes and particleboard were also cut to size. The wood stain board and particleboard had their edges sealed with sodium silicate. The "wet" materials (caulk, adhesive, floor wax, and wood stain) were placed in the chamber shortly after being applied to the sample substrate. The test start (time = 0) was established when the door to the chamber was closed. The first sample was collected within 30 minutes of the start. The samples were collected on Tenax/charcoal and analyzed by GC/FID. The organic species quantified depended on the results of the headspace analysis; total measured organics were also determined and recorded. The duration of each test depended on the

type of material being tested; generally, tests were concluded when the same chamber concentration was observed for several measurements (i.e., at "equilibrium").

Experimental results

Organic compounds identified

Table 1 shows representative organic compounds identified by headspace analysis for several materials.

Table 1: Organic compounds identified via GC/MS

Material/Product	Major Organic Compounds Identified
Latex Caulk	Methyl ethyl ketone, butyl propionate, 2-butoxyethanol, butanol, benzene, toluene
Floor Adhesive (water based)	Nonane, decane, undecane, dimethyloctane, 2-methylnonane, dimethylbenzene
Particleboard	Formaldehyde, acetone, hexanal, propanol, butanone, benzaldehyde, benzene
Moth Crystals	p-Dichlorobenzene
Floor Wax	Nonane, decane, undecane, dimethyloctane, trimethylcyclohexane, ethylmethylbenzene
Wood Stain	Nonane, decane, undecane, methyloctane, dimethylnonane, trimethylbenzene
Latex Paint	2-Propanol, butanone, ethylbenzene, propylbenzene, 1,1'-oxybisbutane, butylpropionate, toluene
Furniture Polish	Trimethylpentane, dimethylhexane, trimethylhexane, trimethylheptane, ethylbenzene, limonene
Polyurethane Floor Finish	Nonane, decane, undecane, butanone, ethylbenzene, dimethylbenzene
Room Freshener	Nonane, decane, undecane, ethylheptane, limonene, substituted aromatics (fragrances)

Emission rates

-Data analysis - Models have been developed to evaluate the data obtained from the chamber tests (2, 3). These models contain rate constants that account for source emission rates, air exchange, the effect of chamber concentration on emissions, and "sink effects" (i.e., material adsorbing on and being released from the chamber walls). The models are used to "fit" the experimental data from the test chambers, and calculations are made of source emission factors.

Effects of environmental variables - As discussed above, a number of environmental variables affect source emission rates. Table 2 shows the effect of Air Exchange Rate and Temperature on the emission factors for para-dichlorobenzene from moth crystal cakes. Both variables show a positive effect on emission rates.

Table 2: Moth crystal emission factors, p-dichlorobenzene (ug/cm^2-hr)

Air Exchange Rate (hr^{-1})	T = 23°C	T = 35°C
0.25	1250	4600
0.5	1400	4850
1.0	1750	5700
2.0	2000	6700

For "wet" materials, Time (or sample age) is a critical parameter. Figure 1 shows the emission factor of total measure organics from a caulking compound over time for two air exchange rates. Note that the emission rate decreases rapidly with time as the volatile solvent materials are depleted from the caulk. Figure 1 also shows that emission rates are initially higher for the high air exchange rate (1.84/hr); after 2 hours, the rates are higher for the low air exchange rate (0.36/hr). Thus, the high air exchange rate caused the source to be depleted quicker.

Within the mixture of organic compounds emitted from a given source, the differences in emission factors for individual compounds can be quite large. Figure 2 shows emission factors over time for three of the compounds emitted from caulk. Note the differences in the emission rates between the compounds at any point in time; also, note that the ketone emission rate decreases much faster than the rates of the other two compounds. This time variation in emission factors for individual compounds will impact the concentrations of these compounds over time. Thus, the absolute (and relative) concentration of a specific compound from a given source changes with time. Figure 3 illustrates this concept by showing the concentration over time for five compounds emitted from a liquid floor wax.

Chamber "sink effects"

Even though the test chambers are constructed of polished stainless steel to minimize reactions with and adsorption on the walls, chamber "sink effects" occur. Measurements of significant chamber "background" levels of organics after testing showed that thorough cleaning of the chambers is required prior to introduction of new samples. In some cases, several cleaning cycles are necessary. Figure 4 illustrates the "sink effect" by showing the predicted mass of organics adsorbed on the chamber walls for the caulking compound. Curves of cumulative mass emitted from the caulk and from the chamber, and the mass of organics in the chamber air, are also provided. Figure 4 illustrates that, even though the source (caulk) emissions occur very rapidly, the "sink effect" can significantly lengthen the time required to fully remove the emissions from the chamber. Note that the caulk emission rate is obtained by determining the slope of the source emissions curve (the top curve in Figure 4).

Conclusions

Determination of emission rates of sources of indoor organics via small chamber testing requires consideration of environmental variables (i.e., temperature, relative humidity, air exchange rate, and time) and the influence of the chamber (concentration and wall effects). Models are useful tools for evaluating the effect of these variables on emission factors. For "wet" materials, emission factors vary significantly with time. For a given material, emission factors for individual compounds can be quite different, and their variation over time may change. Chamber "sink effects" can be significant and should be accouted for when determining source emission factors. Source emission factors determined from chamber tests can be used in ventilation/ dispersion models to provide information on exposures in indoor environments. Validation of this approach awaits experiments in test homes or the field.

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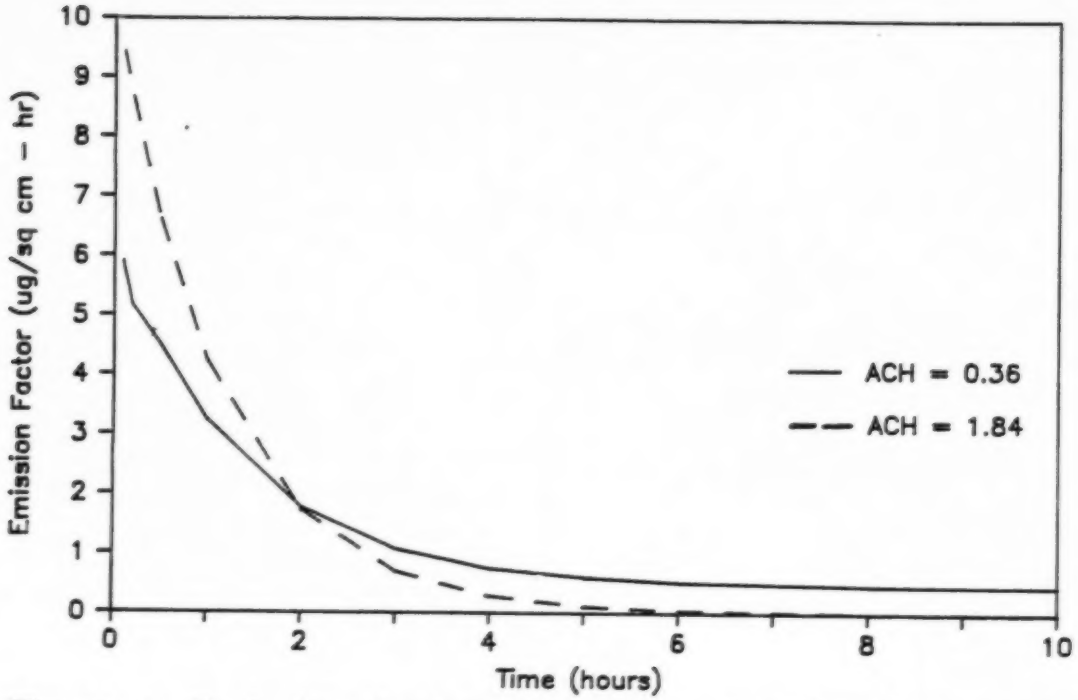

Figure 1. Emission Factor vs Time – Caulking Compound
Total Measured Organics

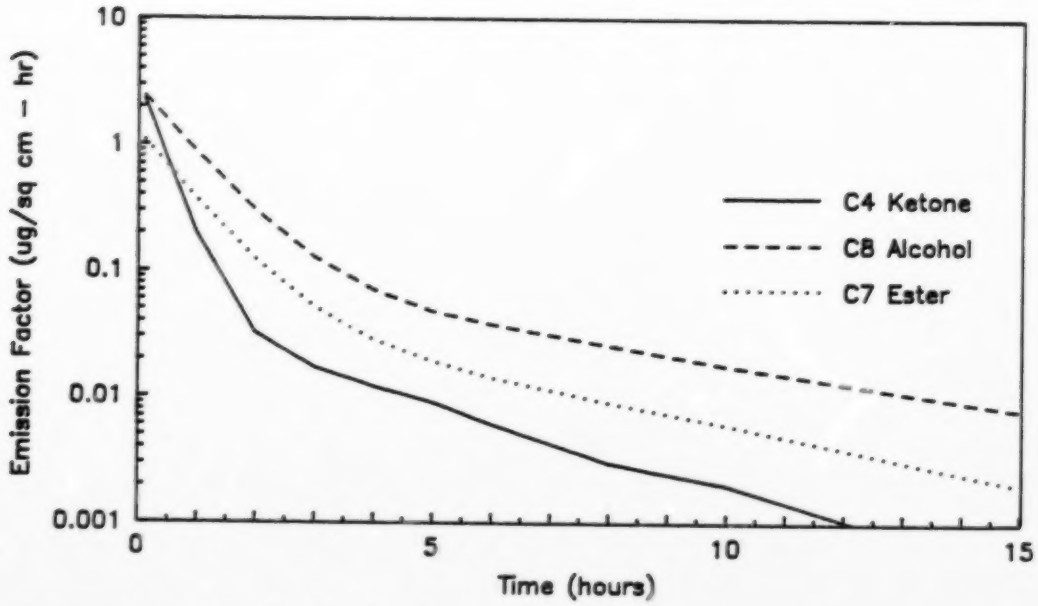

Figure 2. Caulk Emissions vs Time – Three Compounds
T = 23°C; RH = 50%; ACH = 0.36

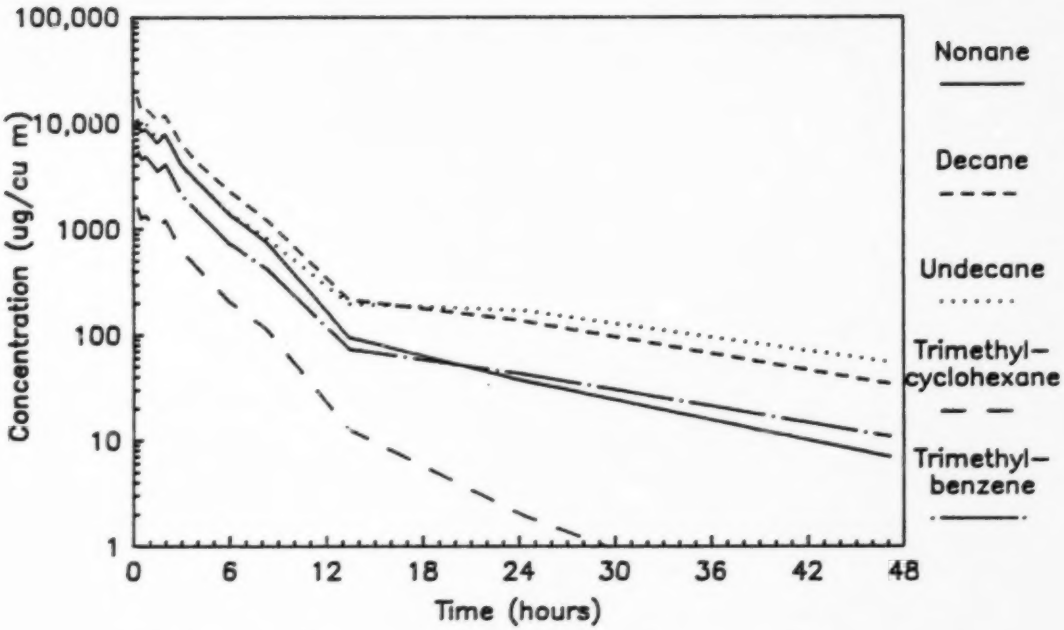

Figure 3. Concentration vs Time – Floor Wax

T = 22°C; RH = 50%; ACH = 0.5

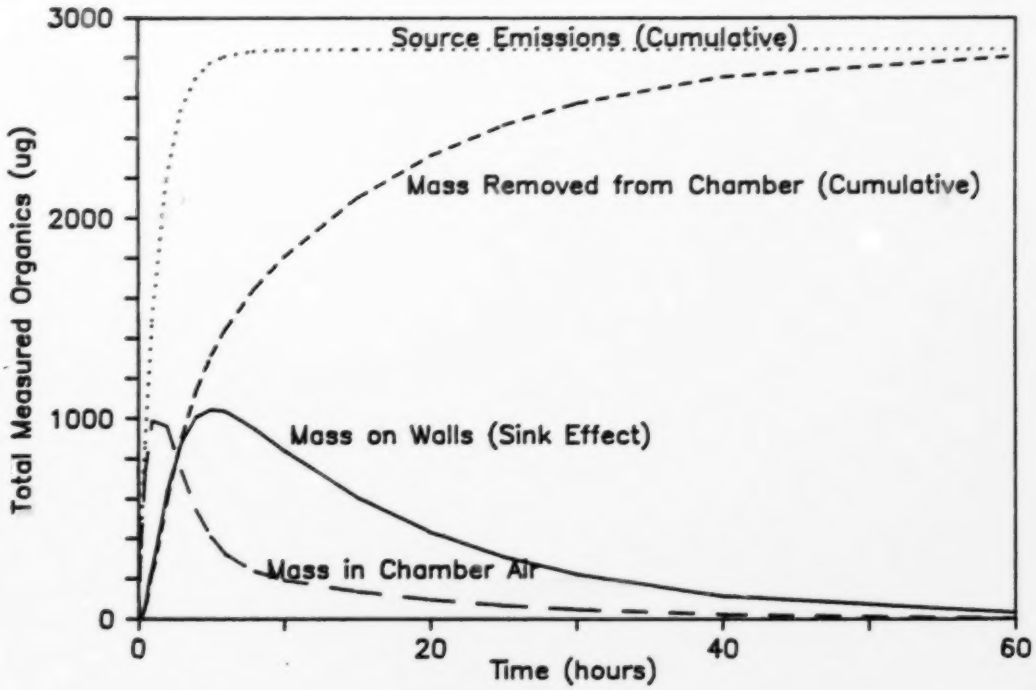

Figure 4. Chamber "Sink Effect" – Caulking Compound

T = 23°C; RH = 50%; ACH = 0.36